UNITED NATIONS

SECRETARIAT

ST

GENERAL

ST/SOA/SER.K/5
24 September 1951

ORIGINAL: ENGLISH

THE ASSAY, CHARACTERISTICS, COMPOSITION, AND ORIGIN OF OPIUM

No. 5

The Ratio of Narcotine to Meconic Acid in Relation to the Origin of Opium (Preliminary Report from the Government Laboratory, London, England)

By J.R. Nicholls and E.G. Kellett

In continuation of the international programme of scientific research undertaken pursuant to resolution 246 F (IX), adopted by the Economic and Social Council on 6 July 1949, the Secretary-General is now publishing three articles, Nos. 5, 6, and 7 in this series, on the determination of narcotine and meconic acid in opium. These three articles present three different methods successively worked out at the Government Laboratory, London, England. While the third method to a great extent supersedes the first two, the Secretary-General considers that the first two methods include features which may be suggestive and helpful to the chemists working on opium, and that they are so different from the third method as to warrant separate publication. Moreover, the substances hindering complete precipitation of narcotine or meconic acid are also dependent on the type of opium and its origin. Thus, although the first method, which is presented in this paper, was hardly more than preliminary, it yielded results more obviously indicative of origin than the methods later developed which are more accurate for narcotine and meconic acid. For this reason the present method still deserves consideration in relation to the origin problem.

THE RATIO OF NARCOTINE TO MECONIC ACID IN RELATION OF THE ORIGIN OF OPIUM

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1. Work at first was carried out on extracts of opium in N/5 hydrochloric acid (5 g. opium to make 50 ml of extract) with the object of getting all the alkaloids and meconic acid into solution, with a minimum of gummy matter.

2. The most promising early results were based on two observations:

   (a) When the extract is adjusted to 30-40% alcohol by volume and saturated with $NaHCO_3$, narcotine crystallizes out nearly pure.

   (b) When the mother-liquor from this separation is made strongly alkaline with NaOH, trisodium meconate crystallizes out. This salt titrates as a mono-acid base to brom-phenol blue.

3. Figures for narcotine and meconic acid obtained in this way are not absolutes. Narcotine has a small but not wholly negligible solubility in 40% alcohol. The solubility of trisodium meconate in aqueous alcohol is considerable, but is much reduced by the presence of excess NaOH. By working in specified conditions on different opium samples, however, figures for the narcotine/meconic-acid ratio have been obtained, which appear to be reasonably characteristic of any one of the types examined, and sufficiently different between different types to constitute a ground for diagnosis. Advantages of the procedure are its simplicity, and the fact that, since the diagnostic figure is a ratio, no confusion can be caused by an unusual amount of water or other inert diluent in the opium.

4. Results obtained were as follows:

	Sample	Narcotine/Meconic-acid (in 40% ethanol)
Turkey	1	.69
"	2	.70
"	3	.73
"	4 (League of Nations IV)	.76
India	1 (Ghazipur)	2.03
"	2 (")	2.33
"	3 (Malwa)	2.02
"	4 (League of Nations I)	2.65
"	5 (League of Nations II)	2.90
Yugoslavia	1	1.28
"	2 (League of Nations V)	1.24
Iran	1	1.52
"	2	1.37
"	3	1.41
"	4 (League of Nations III)	in 50% methanol 1.38
		in 33% ethanol 1.60

/5. The apparent

5. The apparent spread is comparatively wide on the Indian samples where the meconate figure is lowest, because the solubility of trisodium meconate makes a proportionately large effect on a small figure; but, as far as we have gone, it appears that any narcotine/meconic-acid ratio greater than 2 is evidence of Indian origin.

6. With regard to the Iranian opium "League of Nations III", see the Experimental Part, paragraph 11.

EXPERIMENTAL

7. About 5 gm. opium are weighed out, and triturated in a mortar with 20 ml N/5 HCl. The liquid is poured into a stoppered vessel, followed by two further 10 ml portions of N/5 HCl which are worked in the mortar so as to leave it finally clean. The vessel is shaken at intervals for three hours or more, and the contents filtered with suction (a filter-aid is sometimes of advantage). The solid matter is stirred with 10 ml fresh N/5 acid and filtered into the first filtrate.

8. To the filtrate is added 2/3 of its volume of ethanol, and $NaHCO_3$ until a little remains undissolved. The liquid is stirred at intervals for an hour or more, and filtered; about 1 gm. of solid NaOH is added to the filtrate and stirred until dissolved, and the liquid is set aside for 24 hours.

9. The solid residue from the $NaHCO_3$ treatment is washed with 40% ethanol until the washings are colourless, then transferred to an open dish and dried by evaporating down with acetone. It is then extracted with three 10 ml portions of cold chloroform. The filtered chloroform extract, evaporated and dried at 80°C, yields white crystalline narcotine, m.p. usually 170° (pure narcotine 174°).

10. The liquid containing the NaOH, after standing, is filtered; the solid residue is well washed with 4:1 acetone-water, and should be a granular powder of a clean lemon-yellow, dissolving in water to a clear yellow solution which is titrated with N/10 acid to bromphenol blue. Meconic acid = titration x 0.020.

11. Of the fifteen authenticated samples we have so far been able to obtain, only one gave any trouble, namely the Persian "League of Nations III".

In the meconate separation, this gave a copious brown sticky deposit which obviously could not be treated as pure trisodium meconate. A satisfactory product was obtained by working with extract: ethanol 2:1 instead of 3:2. This would probably be satisfactory in all cases.